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ANTIOXIDANTS FOR LUBRICATING OILS

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This invention relates to lubricating oils and more particularly to new antioxidants for various types of lubricating oils.

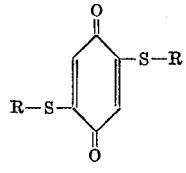
As the present day automobiles are designed to operate at higher and higher speeds and temperatures, and as the jet engines of aircraft are designed to operate at higher temperatures and altitudes, the lubricating oils employed in their operation are subjected to more and more severe requirements and stringent conditions with consequent greater susceptibility to oxidation. This oxidation in turn results in viscosity increase and the formation of acids and sludges and similar oxidation products which corrode the metals which are in contact with the lubricants, plug oil lines and filters, and thus interfere appreciably and disadvantageously with efficient equipment operation.

A wide variety of antioxidants, including compounds such as N-phenyl-1-naphthylamine and phenothiazine have been proposed for and used in lubricating oils but many, such as the former, have been found to be ineffective in some oils while others, such as the latter, have been criticized as having a tendency to form insoluble residues or "dirt" during use.

It is an object of this invention to overcome the disadvantages of the prior art and to provide new and effective antioxidants for various types of lubricating oils.

Other objects and advantages of this invention will be apparent from the following specification.

It has now been found that certain 2,5-disubstituted thio-p-benzoquinones are antioxidants for both synthetic ester type and mineral lubricating oils. The antioxidants of this invention have the following structure:



where R=alkyl or cycloalkyl group of up to about 18 carbon atoms including straight and branched chain alkyl groups and cycloalkyl groups of 4 to 6 carbon atoms, with or without one or more lower alkyl side chains; an aryl or alkylated aryl group of up to about 18 carbon atoms, particularly phenyl and phenyl with one or more lower alkyl substituents; a heterocyclic group of 3 to 5 carbon atoms and 1 or 2 heterocyclic atoms such as nitrogen, oxygen or sulfur. Illustrative of the compounds coming within the scope of this invention are:

2,5-dibutylthio-p-benzoquinone
2,5-diphenylthio-p-benzoquinone
2,5-diethylthio-p-benzoquinone
2,5-bis(2-ethylhexylthio)-p-benzoquinone
2,5-didodecylthio-p-benzoquinone
2,5-dioctadecylthio-p-benzoquinone
2,5-dicyclohexylthio-p-benzoquinone
2,5-di-m-tolylthio-p-benzoquinone
2,5-di-p-tolylthio-p-benzoquinone
2,5-bis(2,4-xylylthio)-p-benzoquinone
2,5-di-p-tert-butylphenylthio-p-benzoquinone

2,5-di-p-octylphenylthio-p-benzoquinone
2,5-bis(1-naphthylthio)-p-benzoquinone
2,5-bis(2-thiazolylthio)-p-benzoquinone
2,5-bis(2-benzothiazolylthio)-p-benzoquinone
2,5-bis(2-benzoxazolylthio)-p-benzoquinone

Of these antioxidants, 2,5-dibutylthio-p-benzoquinone and 2,5-diphenylthio-p-benzoquinone are preferred.

One of the advantages of the antioxidants of this invention resides in the fact that they are effective and may be used either alone or in combination with other common additives such as metal deactivators, corrosion inhibitors, detergents, viscosity index improvers, pour point depressants and other antioxidants.

The lubricating compositions of the invention contain a major amount of mineral or synthetic lubricating oil and a minor amount of the specified antioxidant, the latter being present in an oxidation inhibiting amount. The concentration of the antioxidant to be used for the most effective results depends upon the oil and its particular application. Generally the concentration falls within a range of about 0.05 to 5% by weight of the oil to be protected, although somewhat lower and higher concentrations can be used with at least some of the benefits of the invention being obtained. The preferred range is about 0.1 to 3%.

Synthetic lubricants of the carboxylic acid ester type, i.e. saturated compounds with low freezing points, are finding increased use for various applications such as lube oils for aircraft turbine engines and the antioxidants of this invention are highly efficient in protecting such oils against oxidation which otherwise is often severe under the conditions of operation. Synthetic lubricants of this class include diesters (from reaction of a dibasic acid with an alcohol or of a glycol with a monobasic acid), triesters of trimethylol propane, pentaerythritol esters and low molecular weight polyesters. Examples of such oils include: bis(2-ethyl-hexyl)sebacate; bis(2,2,4-trimethylpentyl)azelate; 2-ethyl-2-butyl-1,3-propanediol dipelargonate; 2,2,4-trimethyl-1,3-propanediol dipelargonate; 2,4-diethyl-2,4-dimethyl - 1,3 - cyclobutanediol dipelargonate; trimethylolpropane triheptanoate; pentaerythritol tetrahexanoate; and a polyester (700 to 2,000 mol. wt.) of neopentyl glycol plus azelaic acid terminated with 2,2,4-trimethylpentanol.

Mineral oils normally employed today such as in automotive and aircraft engine lubrication, are likewise most advantageously affected by the antioxidants of this invention. The various viscosity grades of oils obtained from different crude oil sources and by various treating processes may be protected according to this invention, these oils varying in viscosity for example from 10 to 200 centistokes at 100° F. Typical oils include steam turbine oils, gear oils and the various grades of automotive crank case oils.

A suitable general procedure for the production of the antioxidants of this invention is illustrated by the following description of the preparation of 2,5-bis(butylthio)-1,4-benzoquinone, one of the preferred antioxidants.

To a solution of 81 g. (0.75) mole of 1,4-benzoquinone in 500 ml. of hot ethanol was added a solution of 45 g. (0.50 mole) of butyl mercaptan in 50 ml. of ethanol. This mixture was held at 5° C. for 24 hours and filtered. The product was washed on the filter with warm methanol and then air dried. The desired compound was obtained as a red-brown crystalline solid, M.P. 166°–169° C. Analysis, wt. percent: found, 59.05% C, 7.32% H, 22.25% S; theory, 59.15% C, 7.04% H, 22.54% S.

The following examples will serve to illustrate, in detail, how this invention may be practiced and will show the high degree of effectiveness and activity of the materials of this invention.

Example 1

This example shows the utility of the subject antioxidants in ester-type synthetic lube oils. The oxidation test used was Method 5308.4 of Federal Test Method Standard No. 791. This method is widely used in evaluating aircraft jet lubes. Briefly, the test involves bubbling air at 5 liters per hour through a 100 ml. of oil sample in a glass tube at 347° F. Five 1" x 1" x 0.032" metal coupons (steel, copper, aluminum, magnesium, and silver) are immersed in the oil. Periodically, acid number is determined by ASTM Method D974. The life or induction period of the oil is calculated as the time in hours to an acid number increase of 2.0.

The oil used in this example was a commercial sample of bis(2-ethylhexyl)sebacate; its initial acid number was 0.12. This formulation had an induction period of <10 hours by the above oxidation test just previously described. However, addition of 0.25 wt. percent of one of the subject antioxidants, 2,5-di-tert-butylthio-p-benzoquinone, to this formulation raised the induction period to 65 hours.

Example 2

Following the identical procedure and using the same oil described in Example 1, but using 0.25 wt. percent of 2,5-diphenylthio-p-benzoquinone instead of the antioxidant used in Example 1 resulted in raising the induction period to 40 hours.

Example 3

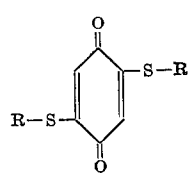
This example demonstrates the potency of the subject antioxidants in mineral oil. The test consisted of bubbling air at 1.25 liters/hour through a 25 ml. oil sample which contained a ¾" x 0.032" copper washer (¼" hole) at 347° F. Acid numbers and induction period were determined as in Example 1. The oil was a commercial paraffinic base mineral oil used in formulating automotive crankcase oils (viscosity=23.82 centistokes at 100° F. and 4.29 centistokes at 210° F.; flash point=380° F.; initial acid number—0.02.) This oil had an induction period of only 13 hours to an acid number increase of 2.0. Addition of 1.0 wt. percent of the subject antioxidant, 2.5-diphenylthio-p-benzoquinone, increased the induction period to 60 hours.

Generally similar results are obtained by the use of other 2,5-disubstituted thio-p-benzoquinones hereinbefore described, i.e., the induction period is increased in synthetic ester type and mineral lubricating oils from 10 or less to 40 or more hours.

Although the present invention has been described with preferred embodiments, it is to be understood that modifications and variations may be made without departing from the spirit and scope of the invention.

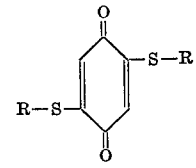
We claim:

1. A process for improving the oxidation resistance of mineral and synthetic ester type lubricating oils which comprises incorporating in the oil as an antioxidant a 2,5-disubstituted thio-p-benzoquinone having the structure:



where R=a C_1 to C_{18} alkyl or cycloalkyl group; an aryl or alkylated phenyl group; or a heterocyclic group of 3 to 5 carbon atoms and 1 or 2 nitrogen, oxygen or sulfur heterocyclic atoms.

2. A process for improving the oxidation resistance of mineral and synthetic ester type lubricating oils which comprises incorporating in the oil from 0.05 to 5% by weight of the oil to be improved of as an antioxidant a 2,5-disubstituted thio-p-benzoquinone having the structure:



where R=a C_1 to C_{18} alkyl or cycloalkyl group; a phenyl or alkylated phenyl group; or a heterocyclic group of 3 to 5 carbon atoms and 1 or 2 nitrogen, oxygen or sulfur heterocyclic atoms.

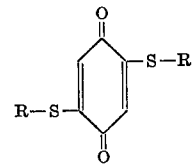
3. A process for improving the oxidation resistance of mineral and synthetic ester type lubricating oils which comprises incorporating in the oil from 0.05 to 5% by weight of the oil to be improved of 2,5-diphenylthio-p-benzoquinone.

4. A process for improving the oxidation resistance of mineral and synthetic ester type lubricating oils which comprises incorporating in the oil from 0.1 to 3% by weight of the oil to be improved of 2,5-diphenylthio-p-benzoquinone.

5. A process for improving the oxidation resistance of mineral and synthetic ester type lubricating oils which comprises incorporating in the oil from 0.05 to 5% by weight of the oil to be improved of 2,5-ditertiarybutylthio-p-benzoquinone.

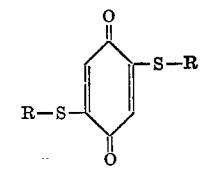
6. A process for improving the oxidation resistance of mineral and synthetic ester type lubricating oils which comprises incorporating in the oil from 0.1 to 3% by weight of the oil to be improved of 2,5-ditertiarybutylthio-p-benzoquinone.

7. A lubricant comprising a major proportion of a mineral lubricating oil blended with about 0.05 to 5% by weight of the oil of a 2,5-disubstituted thio-p-benzoquinone antioxidant having the structure:



where R=a C_1 to C_{18} alkyl or cycloalkyl group; a phenyl or alkylated phenyl group; or a heterocyclic group of 3 to 5 carbon atoms and 1 or 2 nitrogen, oxygen or sulfur heterocyclic atoms.

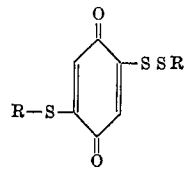
8. A lubricant comprising a major proportion of a synthetic ester type lubricating oil blended with about 0.05 to 5% by weight of the oil of a 2,5-disubstituted thio-p-benzoquinone antioxidant having the structure:



where R=a C_1 to C_{18} alkyl or cycloalkyl group; a phenyl or alkylated phenyl group; or a heterocyclic group of 3 to 5 carbon atoms and 1 or 2 nitrogen, oxygen or sulfur heterocyclic atoms.

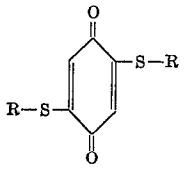
9. A lubricant comprising a major proportion of a mineral lubricating oil blended with about 0.1 to 3% by

weight of the oil of a 2,5-disubstituted thio-p-benzoquinone antioxidant having the structure:



where R=a C_1 to C_{18} alkyl or cycloalkyl group; a phenyl or alkylated phenyl group; or a heterocyclic group of 3 to 5 carbon atoms and 1 or 2 nitrogen, oxygen or sulfur heterocyclic atoms.

10. A lubricant comprising a major proportion of a synthetic ester type lubricating oil blended with about 0.1 to 3% by weight of the oil of a 2,5-disubstituted thio-p-benzoquinone antioxidant having the structure:



where R=a C_1 to C_{18} alkyl or cycloalkyl group; a phenyl or alkylated phenyl group; or a heterocyclic group of 3 to 5 carbon atoms and 1 or 2 nitrogen, oxygen or sulfur heterocyclic atoms.

11. A lubricant comprising a major proportion of a mineral lubricating oil blended with about 0.05 to 5% by weight of the oil of 2,5-diphenylthio-p-benzoquinone.

12. A lubricant comprising a major proportion of a mineral lubricating oil blended with about 0.05 to 5% by weight of the oil of 2,5-ditertiary butylthio-p-benzoquinone.

13. A lubricant comprising a major proportion of a mineral lubricating oil blended with about 0.1 to 3% by weight of the oil of 2,5-diphenylthio-p-benzoquinone.

14. A lubricant comprising a major proportion of a mineral lubricating oil blended with about 0.1 to 3% by weight of the oil of 2,5-ditertiarybutylthio-p-benzoquinone.

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